(19) Japan Patent Office (JP)

(11) Japanese Unexamined Patent S61-168698

(12) Japanese Unexamined Patent Application Publication (A)

(51) Int. Cl.[4]	Identification symbols	JPO file number
C 11 D 3/386		6660-4H
C 12 N 9/96		7421-4B

(43) Publication date July 30, 1986

Status of examination: Not yet requested No. of claims: 1 (Total of 5 pages)

(54) Title of the Invention Composite enzyme granules for detergent

(21) Application number S60-8439

(22) Date of application January 22, 1985

(72) Inventor Takashi ONOUCHI 4-18-20, Kamiuma, Setagaya-ku Tokyo, Japan

(72) Inventor Yorikatsu HOHOKABE 3-20-9, Todoroki, Setagaya-ku Tokyo, Japan

(71) Applicant Showa Denko K.K. 13-9, Shiba Daimon 1-chome, Minato-ku Tokyo, Japan

(74) Representative Kiyotaka SASAKI, 3 others
Patent Attorney

Specifications

1. Name of the Invention

Composite enzyme granules for detergent

2. What is Claimed is:

1. Composite enzyme granules for detergent, wherein a core portion containing a protease is coated with a shell portion containing a lipase and/or an amylase.

2. The composite enzyme granules for detergent according to Claim 1, wherein the core portion contains:

(a) 2 to 40% by weight of a protease, and

(b) 0.5 to 20% by weight of a water-soluble calcium salt component,

with respect to the composite enzyme granules.

3. The composite enzyme granules for detergent according to Claim 1, wherein the shell portion contains:

(c) 2 to 40% by weight of a lipase and/or an amylase, and

(d) 0.5 to 30% by weight of a component of a nonionic surfactant,

with respect to the composite enzyme granules.

4. The composite enzyme granules for detergent according to Claims 1, 2 or 3, wherein the shell portion is further coated with a protective layer.

3. Detailed Description of the Invention

[Industrial Field of the Invention]

This invention relates to composite enzyme granules for detergent and, more specifically, composite enzyme granules for detergent comprising a protease, a lipase and/or an amylase in which inactivation of the enzymes is suppressed.

[Prior Art]

Stains on clothing resulting from wear are slightly different depending on the region of the human body; however, 40 to 70% of fats and 10 to 40% of proteins exist as an organic scurf. Moreover, a large amount of starch is often contained in stains of food, etc. [Fragrance Journal, No.42, Pages 43-50 (1980)]. Washing of these stains using a regular detergent combined with a surfactant along with a builder may not be sufficient, but it is known that the washing effect is remarkably enhanced through concomitant use with an enzyme [Journal of the Japan Research Association for Textile End-Uses, Vol. 11, No. 5, Pages 280 to 290(1970)]. Among enzymes, detergents comprising a

protease that degrades proteins have already been well-established [Fragrance Journal No. 53, Pages 89 to 95 (1982)] and the applicant of the present application proposes a granule enzyme composition, etc. in which inactivation of the protease is suppressed (Patent Application No. SHO 59-155188).

The effect of a detergent comprising an amylase, which is a starch degradation enzyme, and a lipase, which is a fat degradation enzyme, has also been confirmed [The 15th Symposium on Washing, Study Report No. 6 on Washing of Oil and Fat Stains by Lipase, Japan Oil Chemists' Society (October 18, 1983)].

Therefore, composite enzyme detergents comprising an enzyme such as a lipase or an amylase, etc. as well as a protease are extremely useful.

Composite enzyme formulations are prepared by a similar technique as that for conventional single enzyme formulations. For example, a single enzyme formulation is produced by granulating dry enzyme powder or a concentrated enzyme solution as an enzyme material, a cellulose powder, a salt powder, and a binder, etc. using a granulator (Japanese Published Examined Application No. SHO 58-26315), but a composite enzyme formulation is also produced using dry enzyme mixture powder or a concentrated enzyme mixture solution prepared by mixing different types of enzymes.

Conventional composite enzyme formulations produced as described above have the following problems.

(1) A protease degrades proteins, but because enzymes are types of proteins, a protease also degrades lipases and amylases, etc. Therefore, when granulating using an enzyme ingredient or a concentrated enzyme solution prepared simply by mixing a protease with other enzymes, part of the lipase and amylase, etc. is degraded by the protease during granulation and their functions may not be sufficiently exerted. In other words, if an enzyme formulation granulated using enzyme powder or a concentrated enzyme solution prepared by mixing a protease with other enzymes is preserved under conditions of high temperature and high humidity, the enzymes partially become active due to the water absorbed into the granules, the added lipase or amylase are partially degraded by the protease, and the enzymatic titers may remarkably decrease. This is the cause of a decrease in enzymatic titer when a composite enzyme formulation is blended with a detergent and preserved, and the planned effect of the enzymes becomes insufficient, decreasing the detergency.

(2) In enzyme formulation, in order to prevent the decrease in enzymatic titer during preservation, measures for stabilizing enzymes are taken, but the conditions for stabilization differ depending on the enzyme. Therefore, when an enzyme ingredient or a concentrated enzyme solution prepared by simply mixing different types of enzymes is used, granulation under conditions suitable for stable preservation of each enzyme cannot always be conducted, and the actual situation is that granulation is conducted under conditions using the highest common factor of each enzyme.

(3) A protease may cause inflammation on the mucosa of human bodies [FDA, PB204118 (1971)], and therefore it is required that an enzyme formulation containing a protease be less quickly formed into dust. Regarding enzyme formulations that are hardly formed into dust, there are various proposals [e.g., Fragrance Journal No. 42, Pages 43 to 50 (1980)] and the amount of a protease formed into dust has decreased to a large degree, but it cannot be said to be perfect.

[Problems to be Solved by the Invention]

The objective of the present invention is to provide composite enzyme granules for detergent in which degradation of other enzymes by a protease does not occur and each enzyme retains its titer for a long period of time, and the protease is not formed into dust.

[Means for Solving the Problems and Effect]

The inventors of the present application found that the above objective could be achieved by a structure in which the core containing a protease is coated with a layer of other enzymes, and completed the present invention.

In other words, the present invention relates to composite enzyme granules for detergent

in which a core portion containing a protease is coated with a shell portion containing a lipase and/or an amylase and a protective layer is further provided on the surface, if desired.

Each portion of the composite enzyme granules for detergent of the present invention will be described below.

Core portion

The core portion contains a protease that is active under use conditions as a detergent. As the protease, for example, subtilisin Carlsbers, subtilisin EPN, and API-21 (refer to Japanese Published Unexamined Application No. SHO 58-134990), etc. are suitable. The used amounts of these enzymes are different depending on the enzymatic titer, but as general enzyme powder, 2 to 40% by weight is used with respect to the composite enzyme granules.

Moreover, 0.5 to 20% by weight of a water-soluble calcium salt as an essential component for stabilization of the protease is contained in the core portion with respect to the composite enzyme granules. As the calcium salt, any calcium salt other than water-insoluble calcium salts can be used, but examples of particularly preferable calcium salts among these include calcium chloride, calcium sulfate, calcium dihydrogenphosphate, calcium nitrate, calcium acetate, calcium citrate, calcium gluconate, and calcium succinate, etc.

Other additive components that do not affect the stability of the enzymes can also be used for the core portion if desired in addition to the above essential components. As such components, firstly, (1) in order to improve the granulation property and aid improvement of the stability of the enzymes in the granules, a nonionic surfactant can be contained.

Examples of the nonionic surfactant include polyoxyethylene (or propylene), alkyl, alkenyl or phenyl ethers, and polyoxyethylene (or propylene) higher fatty acid esters, etc.

Moreover, (2) for the purpose of improving the granulation property and enhancing the stability of the enzymes in the granules, an appropriate amount of a sodium salt of an α-olefin sulfonic acid (trivial name: AOS) obtained from an α-olefin having 10 to 20 average carbon atoms and/or a sodium salt of sulfuric acid alkyl polyoxyethylene (trivial name: AES) obtained from an alcohol having 8 to 20 average carbon atoms can also be used.

Further, (3) as a disintegrating agent or an extender for promoting the solubility at the time of use as a detergent, up to 20 to 90% by weight of a water-soluble alkali metal salt is used. Examples of such an alkali metal salt include, for example, sodium sulfate, potassium sulfate, sodium chloride, potassium chloride, disodium citrate, monosodium citrate, and sodium tripolyphosphate, etc.

Moreover, (4) as a stabilizer for the granulation property and the enzymes in the obtained granules, an inactivated enzyme protein, a protein obtained together with the active enzyme in a culture or separation process, and other proteins such as soybean protein, soybean casein, and milk casein, etc. may be used.

(5) TiO_2, etc. as a brightening agent, carboxymethylcellulose, etc. as a binder, and polyethylene glycol, etc. as a coating agent may also be used accordingly.

Shell portion

In the shell portion, 2 to 40% by weight of a lipase-containing enzyme powder and α-amylase-containing enzyme powder, etc. generally used for detergents is used with respect to the total weight of the composite enzyme granules. Moreover, in order to improve the granulation property and enhance the stability of the enzymes, 0.5 to 30% by weight of the nonionic surfactant described for the core portion is used as an essential component with respect to the composite enzyme granules.

Further, as other additive components, the water-soluble calcium salt, the water-soluble alkali metal salt, various proteins, the bleaching agent, and the binder, etc. described for the core portion are also used.

Protective layer

The preservation property of the composite enzyme granules can be increased by further providing a protective layer to the structure of the core portion coated with the shell portion. The protective layer can be provided

by adding, for example, titania (TiO_4) and talc, etc. to an aqueous polyethylene glycol solution, coating this solution on the surface of the shell portion, and drying.

The use of the composite enzyme granules of the present invention is not limited to an additive agent of a detergent, but may also be used as a spot remover alone. When they are used as an additive agent, they may be mixed in a detergent in advance or may be used as an additive agent for washing using a washing machine.

[Examples]

The composite enzyme granules for detergent of the present invention are described below with reference to Examples and Comparative Examples.

Example 1

Protease API-21-containing enzyme powder (enzymatic titer of 95 n Katal/mg)	: 500 g
Calcium sulfate dehydrate crushed into fine particles	: 60 g
Citric acid soda dihydrate	: 200 g
Sodium sulfate 10 hydrate	: 600 g
Polyoxyethylene lauryl ether powder	: 80 g

The above were charged into a mixing granulator LMA-10 Type manufactured by Nara Kikai Corporation, and were agitated at a rotation rate of 200 rpm for 3 minutes, before being granulated at an agitation rate of 420 rpm while a small amount of distilled water and 140 ml of an aqueous 1 % carboxymethylcellulose solution were added.

The wet granules obtained as described above were dried by a fluidized-bed drier until the water content became 3% and were then sorted with a JIS standard standardized sieve to obtain 850 g of granules having a particle size of 0.3 mm to 0.5 mm. Next, 600 g of these dried granules were put into a centrifugal fluidizing type coating machine (CF-360 manufactured by Freund Corporation), and a small amount of lipase-containing mixture powder having the following composition:

Lipase-containing enzyme powder (titer of 47 u/mg)	300 g
Soybean protein powder (100 meshes or less)	50 g
Sodium sulfate 10 hydrate (100 meshes or less)	30 g
Polyoxyethylene lauryl ether powder	30 g

was added as divided portions together with a binder (320 g of an aqueous 13% PEG 4000 solution) while the mixture was rotated and fluidized at 250 pm at an introduced air temperature adjusted to 35°C, and it was uniformly coated on the surfaces of the granules. After the coated granules were dried by the fluidizing drier until the water content became approximately 3%, they were charged again into the centrifugal fluidizing type coating machine, a small amount of mixture powder of 35 g of titania (TiO_4, 200 meshes or less) and 5 g of talc was added as divided portions together with 100 g of an aqueous 10% PEG6000 solution, it was uniformly coated on the surfaces of the granules, and they were further dried by the fluidizing drier until the water content became 2 to 3%. The enzymatic titers of granules (approximately 1 .0 Kg) having a particle size of 0.5 to 1 .0 mm obtained as described above were 17.5 n Katal/mg for the protease and 12 u/mg for the lipase. Furthermore, for measurement of the titer for the protease, the method described in Japanese Published Unexamined Application No. SHO 58-134990 was used and for measurement of the titer for the lipase, the method described on Pages 230-233 of Enzyme Utility Handbook (edited by Michio Kozaki, Jijin Shokan, June 1980) was used.

Example 2

In the same manner as in Example 1, a mixture having the following composition:

Protease API-21-containing enzyme powder (enzymatic titer of 95 n Katal/mg)	: 500 g
Sodium sulfate 10 hydrate	: 800 g
Calcium sulfate dehydrate crushed into fine particles	: 70 g
Soybean casein	: 50 g

was charged into the mixing granulator and was granulated while a small amount of distilled water was added.

After they were dried until the water content became 3%, 700 g of 0.3-mm to 0.5-mm granules obtained after the sorting process were uniformly coated on the surfaces of the

granules using the centrifugal fluidizing type coating machine with a mixture having the following composition:

α amylase-containing enzyme powder (liquefying power of 2800 Lj/g)	: 400 g
Sodium sulfate 10 hydrate (100 meshes or less)	: 50 g
Citric acid soda dihydrate (100 meshes or less)	: 30 g
Calcium sulfate dehydrate crushed into fine particles	: 10 g

As a binder, a small amount of an aqueous 13% PEG4000 solution was used. After the coated granules were dried, they were charged again into the centrifugal fluidizing coating machine, a mixture of 35 g of titania (TiO_4, 200 meshes or less) and 5 g of talc was uniformly coated on the surface of the particles while an aqueous 10% PEG6000 solution was added, and they were further dried until the water content became 3% or less. The enzymatic titers of granules (approximately 1 .2 Kg) having a particle size of 0.5 to 1.0 mm obtained as described above were 18 n Katal for the protease and 8,500 Lj/9 for the α-amylase.

Furthermore, the measurement of the liquefying power of the α-amylase was conducted in accordance with the test method for amylases for liquefaction of JISK 7001.

Comparative Example 1

The materials listed below:

Protease API-containing enzyme powder (enzymatic titer of 95 n Katal/mg)	: 208 g
Lipase-containing enzyme powder (titer of 47 u/mg)	: 300 g
Sodium sulfate 10 hydrate	: 280 g
Citric acid soda dehydrate	: 83 g
Polyoxyethylene lauryl ether powder	: 64 g
Calcium sulfate dihydrate	: 25 g
Soybean protein powder	: 50 g

were mixed such that the composition of the resulting composite enzyme granules became the same as that of Example 1, charged into the mixing granulator manufactured by Nara Kikai Corporation, and granulated while a small amount of distilled water was added. After drying, a mixture powder of 35 g of titania and 5 g of talc was uniformly coated on the surfaces of the granules together with 100 g of an aqueous 10% PEG6000 solution and dried. The titers of the enzymes of the granules obtained described above were 16.5 n Katal/mg for the protease and 7 u/mg for the lipase.

Comparative Example 2

The materials listed below:

Protease API-21-contaiing enzyme powder (enzymatic titer of 95 n Katal/mg)	: 246 g
α-amylase-containing enzyme powder (liquefying power of 28000 Lj/g)	: 400 g
Sodium sulfate 10 hydrate	: 444 g
Citric acid soda dihydrate	: 30 g
Calcium sulfate dehydrate crushed into fine particles	: 45 g
Soybean casein	: 25 g

were mixed such that the composition of the resulting composite enzyme granules became the same as that of Example 2, charged into the mixing granulator manufactured by Nara Kikai Corporation, and granulated while a small amount of distilled water was added. After drying, a mixture powder of 35 g of titania and 5 g of talc was uniformly coated on the surfaces of the granules together with 100 g of an aqueous 10% PEG6000 solution and dried. The titers of the enzymes of the granules obtained described above were 17 n Katal/mg for the protease and 7500 Lj/g for the lipase.

[Effect of the Invention]

(1) The composite enzyme granules of the present invention have a structure in which a layer portion containing other enzymes, i.e., a lipase and an amylase, etc., is formed around a core containing a protease, whereby the protease is not easily contacted to other enzymes, and they can be produced by granulating protease powder or a concentrated solution thereof, and then with these granules as the core, attaching the other enzymes on the surface in a layer. According to such a production method, because contact of the protease to the other enzymes is avoided, degradation of the lipase and the amylase by the protease at the time of producing the enzyme granules can be substantially prevented.

(2) The composite enzyme granules of the

present invention have a structure in which the protease is not easily contacted to other enzymes, and therefore, if the protease is activated by moisture absorption, etc., degradation of the other enzymes by the protease can be prevented.
(3) Because the core portion containing the protease and the shell portion containing the other enzymes are separately granulated, they can be granulated under optimum conditions for stable preservation of each enzyme, and the quality of the composite enzyme granules can be retained.
(4) In the composite enzyme granules of the present invention, the protease that may cause inflammation of mucosa of human bodies is present within the core portion and the surface thereof is coated with a thick layer containing other enzymes, and therefore, the protease is never formed into dust by normal handling, making them extremely desirable from safety and hygiene standpoints.

Patent agent: (8107) Kiyotaka Sasaki
(3 other persons)
[seal]

File name “JP 61-168698A.pdf”

Line 7 of the upper right column on Page 3/5 of PDF
We believe that “非イオン性界面活性” should be “非イオン性界面活性剤,” so we translated as “非イオン性界面活性剤.”

Line 5 to the bottom of the upper right column on Page 5/5 of PDF
We believe that “蒸留した” should be “造粒した” as in the comparative example 1, so we translated as “造粒した.”